PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6:

C09D 11/16, B44C 1/175

(11) International Publication Number:

WO 98/36031

A1 (43) International Publication Date:

20 August 1998 (20.08.98)

(21) International Application Number:

PCT/US98/02682

(22) International Filing Date:

13 February 1998 (13.02.98)

(30) Priority Data:

08/800,755 08/918,732 14 February 1997 (14.02.97) US

1 August 1997 (01.08.97)

US

(71) Applicant: BINNEY & SMITH INC. [US/US]; 1100 Church Lane, Easton, PA 18044 (US).

(72) Inventors: SANTINI, Andree, F.; 1616 Arrowwood Drive, Easton, PA 18042 (US). MILLER, Richard, E.; LakeSide by the Sea, 83 San Juan Drive, Palm Coast, FL 32137 (US). ROWAN, David; 3970 Oliver Avenue, Bethlehem, PA 18020 (US). LEIDY, Chris; 304 Berks Street, Easton, PA 18045 (US). FOX, Paul; 31 Shorneclife Road, Newton, MA 02158 (US).

(74) Agents: GAGALA, Bruce, M. et al.; Leydig, Voit & Mayer, Ltd., Suite 4900, Two Prudential Plaza, Chicago, IL 60601 (US). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: WASHABLE COLORING COMPOSITION SUITABLE FOR USE IN DRY ERASE MARKERS

(57) Abstract

A washable dry erase coloring composition comprising an acid dye or polymeric dye colorant, a dye vehicle, a release agent, and an anionic dyeblocker. The dyeblocker additive may be an aromatic organic sulfonate and, preferably, is either a sulfonated naphthalene condensation product or a sulfonated phenol-formaldehyde condensation product. The dry erase coloring composition is suitable for use in marking on a whiteboard and enhances fugitivity from skin and fabrics. The dry erase coloring composition may optionally contain a film forming resin. More specifically, the invention is, in one preferred embodiment, a washable erasable whiteboard marker ink comprising an acid dye or polymeric dye, water, a film forming resin, a release agent and an aromatic organic sulfonate. In addition, the invention also includes a method of transferring an image from a whiteboard or non-porous surface to paper. This method comprises the steps of: (a) drawing an image on a whiteboard or non-porous surface with a washable coloring composition containing a dyeblocker; (b) applying a moistened paper to the image; (c) rubbing the moistened paper to transfer the image from the whiteboard to the paper; and (d) removing the paper.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	· Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Мопасо	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	us	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Кепуа	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand	211	Zimbabwe
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

WASHABLE COLORING COMPOSITION SUITABLE FOR USE IN DRY ERASE MARKERS

This application is a continuation-in-part of U.S. Patent Application Serial No. 08/800,755 filed on February 14, 1997, and a continuation-in-part of U.S. Patent Application Serial No. 08/918,732 filed on August 1, 1997.

FIELD OF THE INVENTION

The present invention relates generally to the field of washable dry erase coloring compositions for drawing and coloring purposes. In one particular aspect, the invention relates to writing instruments containing washable liquid coloring compositions, and more specifically to the formulations of coloring compositions for use in markers. Further, washable coloring compositions are provided which are suitable for use on whiteboards.

15

20

10

BACKGROUND OF THE INVENTION

Whiteboards, also known as dry erase boards, are commonly used in offices, schools, and other locations where a chalkboard might otherwise be found. Writings on a dry erase board are erasable by wiping lightly with felt, dry cloth or paper. Suitable whiteboard surfaces generally include a melamine, vinyl, polyethylene laminate, or enamel resin layer affixed to a backing. Such whiteboards are characterized in that they have hard, white surfaces that are very smooth in appearance, and are essentially nonporous. Alternatively, a whiteboard may comprise a sheet of polymeric film such as an acrylic or UV curable resin.

25

A variety of compositions are known for use in writing on impervious writing surfaces such as whiteboards. These coloring compositions suitable for use on whiteboards must erase easily without requiring a comprehensive cleaning. Additionally, the whiteboard compositions must be removable without leaving visible remains commonly termed "ghosting."

30

35

Whiteboard coloring compositions suffer from a variety of well known deficiencies. Most whiteboard markers are alcohol or solvent based which may be toxic and, thus, are not appropriate for use by young children. For example, U.S. Patents 4,954,174, 5,316,574, and 5,324,764 describe erasable ink compositions for writing on an impervious surface that contain an organic solvent such as an alcohol. Further, many whiteboard markers produce writings which are not readily erasable from whiteboards after the passage of a significant period of time.

10

15

20

25

30

Finally, current whiteboard markers have a propensity to leave enduring stains on clothing. While permanence is a desirable characteristic of the so-called "permanent" markers, it is one of the most objectionable properties for coloring instruments used by young children.

Water-based marker compositions have been used. U.S. Patents 5,412,021 and 5,561,175, for example, describe water-based compositions that contain a pigment, a separating agent, and a water-soluble resin. These aqueous compositions, however, lack fugitivity from fabrics and often from skin.

It is therefore one general object of the invention to provide a method of imparting skin fugitivity to a dry erase coloring composition.

Another object is to provide a dry erase coloring composition which, in addition to being washable from skin, exhibits enhanced launderability from fabrics.

A related object is to provide non-toxic, dry erase coloring compositions, such as inks, which are suitable for use by young children who may make marks on themselves and their clothing.

A further object of the invention is to provide a coloring composition suitable for use on whiteboards and other non-porous surfaces which is also washable from the skin and clothes.

An additional object is to provide a process for transferring an image produced by a coloring composition on whiteboards or other non-porous surfaces to paper.

These and other objects and advantages of the present invention, as well as additional inventive features, will be apparent to those skilled in the art from the following description of the invention and the appended claims.

BRIEF SUMMARY OF THE INVENTION

The discovery of the present invention is that one may incorporate into a coloring composition a dyeblocker additive which imparts to the composition dramatically improved fugitivity from skin. At the same time, it has been discovered that, in many instances, the dyeblocker additive will noticeably enhance fugitivity from fabrics ordinarily used in children's clothing and from other surfaces.

In one of its most general aspects, the coloring composition of the invention comprises a colorant selected from the group consisting of an acid dye and a

10

15

20

25

30

35

polymeric dye and a dyeblocker. Generally, dyeblockers suitable for use in the present invention are anionic materials capable of bonding to the dye receptor sites on skin, fabrics, or other surfaces. More specifically, suitable dyeblockers are aromatic organic sulfonates and are preferably selected from the group consisting of a sulfonated naphthalene condensation product and a sulfonated phenolformaldehyde condensation product. The coloring compositions of the invention are easily washed from the skin, and, in addition, are also more easily washed from textiles. In another general respect, the present invention includes a method of imparting skin washability to a dye-containing coloring composition by adding to a coloring composition an effective amount of an anionic dyeblocker. Preferably, the dyeblocker is selected from the group consisting of a sulfonated naphthalene condensation product and a sulfonated phenol-formaldehyde condensation product.

Thus, in one form, the invention is a washable coloring composition comprising an acid dye or polymeric dye colorant, a dye vehicle, a release agent, and an aromatic organic sulfonate such as a sulfonated phenol-formaldehyde condensation product or a sulfonated naphthalene condensation product. This form of the invention is suitable for use in marking on a whiteboard. Preferably, the inventive coloring composition also contains a film forming resin. More specifically, the invention is, in one preferred embodiment, an erasable whiteboard marker ink comprising an acid dye or polymeric dye colorant, water, a film forming resin, a release agent, and a sulfonated phenol-formaldehyde condensation product. Further, a marker containing the coloring composition of the invention is provided.

In another form, the invention includes a method of transferring an image from a whiteboard or non-porous surface such as a plastic laminate to paper by (a) drawing on the whiteboard or other non-porous surface with a washable coloring composition comprising an acid dye or polymeric dye colorant, a dye vehicle, a film forming resin, a release agent, and a dyeblocker; (b) applying a moistened paper to the image on the whiteboard or other non-porous surface; (c) rubbing the moistened paper to transfer the image from the whiteboard or other non-porous surface to the paper; and (d) removing the paper from the whiteboard or other non-porous surface. Alternatively, the inventive method includes images drawn using a washable coloring composition comprising an acid dye or polymeric dye colorant, a dye vehicle, a release agent, and a sulfonated phenol-formaldehyde

BNSDOCID: <WO_____9836031A1_I_>

10

15

20

25

30

35

condensation product or a sulfonated naphthalene condensation product.

DETAILED DESCRIPTION

The washable coloring composition of the present invention comprises an acid dye or polymeric dye colorant, a dye vehicle, a release agent, and an anionic dyeblocker. One suitable class of anionic dyeblockers are aromatic organic sulfonate dyeblockers. Preferably, the dyeblocker is selected from the group consisting of a sulfonated phenol-formaldehyde condensation product and a sulfonated naphthalene condensation product. Preferably, the coloring composition also contains a film forming resin. The washable coloring compositions of the present invention exhibit enhanced fugitivity from skin and fabrics. This coloring composition is suitable for use for marking on whiteboards and may be easily erased by ordinary means with no apparent ghosting.

The dyeblocker component suitable for use in the invention imparts skin fugitivity and, in some instances, enhanced fabric fugitivity to the coloring compositions of the invention. Many substances may suitably perform as a dyeblocker. For example, anionic materials, such as, surfactants or polymers, which contain reactive functional groups, such as, for example, acid groups, may be used. Although the present invention is in no way limited to a mechanism by which dyeblockers operate, it is believed that the acid groups in these anionic materials react with dye-receptor sites present in the skin, fabrics, and other surfaces to form a barrier to dye receptors. Suitable anionic dyeblockers include any straight chain or aromatic compound containing, for example, highly reactive carboxylic, sulfonic, or nitric groups which possibly react with dye-receptor cites such as, for example, amino groups that are commonly present on skin, some types of fabrics, and other surfaces. Preferably, the anionic dyeblocker is an aromatic organic sulfonate. One group of preferred aromatic organic sulfonate dyeblockers are sulfonated phenol-formaldehyde condensation products, sulfonated naphthalene condensation products, or mixtures thereof. The dyeblockers useful in the practice of the present invention do not impair the stability of the coloring compositions of the invention. By stability, it is meant that the coloring composition, which includes the condensation product additive, must not precipitate nor exhibit a marked change in color or pH when maintained at a temperature of 140°F for two weeks. Preferably, dyeblockers selected for use in the invention, in addition to imparting fugitivity from skin, also enhance fugitivity

10

15

20

25

30

35

from textiles and other surfaces. Suitable dyeblockers may often be film-forming, which may further prevent the migration of dyes toward the reactive sites of a substrate, thereby reducing staining.

Sulfonated phenol-formaldehyde condensation product dyeblockers useful in the practice of the invention are described in U.S. Pat. No. 4,501,591. Suitable sulfonated phenol-formaldehyde condensation products may be, but are not limited to, linear, low molecular weight condensation products; that is products having an average molecular weight of less than about 1000, for example, in the range of 250 to 700. Such products are water-soluble and may be prepared by conventional art-recognized techniques, for example, by condensation of formaldehyde with one or more phenols in a mole ratio of about 1.0 to 0.8, phenol(s) to formaldehyde, at a pH of less than 7 using an acid catalyst such as HCl, wherein at least one of the phenols is a phenolsulfonic acid or alkali metal salt thereof. Preferably, the phenols comprise, in addition to the sulfonic acid or salt thereof, a sulfone, for example, dihydroxy aromatic diphenol sulfone. Such condensation products contain, in addition to sulfonic acid groups or alkali metal salts thereof, sulfone groups.

Other sulfonated phenol-formaldehyde condensation products are described in U.S. Patent Re. 33,365, and U.S. Patent Nos. 4,908,149, 4,592,940 and 4,680,212.

One sulfonated phenol-formaldehyde condensation product dyeblocker suitable for use in compositions of the invention is Aerofix NTM, commercially available from Aerochem Corporation. Aerofix NTM is supplied as an aqueous dispersion of the phenol-formaldehyde condensation product containing about 17% by weight active condensation product ingredient. Other sulfonated phenol-formaldehyde condensation products suitable for use in the compositions of the invention are Intratex NTM available from Crompton and Knowles Corporation (dispersion containing about 18% by weight active condensation product ingredient), and Gascofix NYTM available from GCI Technologies, Inc. (dispersion containing about 29% by weight active condensation product ingredient). Compatible mixtures of these sulfonated phenol-formaldehyde condensation products may also be used. The sulfonated phenol-formaldehyde condensation product, Aerofix NTM, is preferred for use in compositions of the invention. Aerofix NTM dramatically enhanced skin washability and fabric launderability in compositions of the invention. Other sulfonated phenol-formaldehyde

10

15

20

25

30

35

condensation products may produce equivalent, or even better, results and are within the scope of the invention.

A sulfonated naphthalene condensation product dyeblocker suitable for use in coloring compositions of the invention is Tamol SNTM. Tamol SNTM is commercially available from Rohm and Haas and is supplied in solid form containing 100% by weight active ingredient. Other sulfonated naphthalene condensation products may produce equivalent, or even better, results and are within the scope of the invention. The various dyeblockers discussed above may be used alone or in combination where the dyeblockers are compatible with one another.

Other suitable dyeblockers for the coloring composition of the invention are anionic surfactants. One such suitable anionic surfactant is Dowfax 8390TM which is commercially available from Dow Chemical Co. Dowfax 8390TM is an alkylated diphenyloxide disulfonate and, more specifically, it is disodium hexadecyldiphenyloxide disulfonate (15-35%) and disodium dihexadecyldiphenyloxide disulfonate (5-10%).

The specific mechanism by which the dyeblocker additive imparts skin fugitivity and enhances fabric fugitivity is not known. However, it is believed that the condensation products tie up the reactive sites of the substrates to which coloring compositions containing the dyeblocker are applied. The dye used as a colorant in compositions of the invention then has a reduced ability to physically or chemically associate with the substrate, be it skin or fabric.

The sulfonated phenol-formaldehyde condensation product Aerofix NTM was tested in numerous water-based dye compositions comprising colorants, preservatives, and humectants. Compositions of the invention should contain a sufficient amount of the sulfonated phenol-formaldehyde condensation product to impart skin fugitivity and enhance fabric fugitivity of the composition.

The amount of dyeblocker additive present in the coloring compositions of the invention depends upon the specific condensation product used. At a minimum, the condensation product must be present in an amount sufficient to impart enhanced skin and fabric fugitivity. This effect is seen with as little as about 1% by weight of the active condensation product ingredient in the total dry erase coloring composition. Even greater washability is achieved when about 3.5% by weight of the active sulfonated phenol-formaldehyde condensation product ingredient is used where the dyeblocker additive is Aerofix NTM. In

general, a greater amount of condensation product additive present in the dry erase coloring composition leads to better washability from fabric, skin and other surfaces. However, at a certain point, the addition of more condensation product does not yield any improvement in the washability of the dry erase composition.

The upper limit of the dyeblocker additive concentration may also be imposed by constraints on the viscosity and the long term stability of compositions of the invention. For example, the dry erase coloring composition cannot have a significantly viscous consistency or it will not flow through a marker nib when used in the form of a marker ink. Accordingly, the concentration of condensation product additive is preferably in an amount of from about 2% to about 15% by weight of the active condensation product ingredient in the total coloring composition.

In general, where the Aerofix NTM dispersion is used, the beneficial effect of the additive occurs at a concentration of at least about 10% by weight of the Aerofix NTM dispersion based on the total coloring composition. Where Aerofix NTM is the selected dyeblocker, it is present in an amount of from about 5% to about 60% by weight of the Aerofix NTM dispersion based on the total coloring composition of the invention. Preferably, the Aerofix NTM component is present in an amount of from about 15% to about 40% by weight of the Aerofix NTM dispersion based on the total coloring composition. Most preferably, about 15% to about 30% by weight of the Aerofix NTM dispersion based on the total coloring composition is used in coloring compositions of the invention.

The coloring compositions of the invention also include one or more colorants. Suitable colorants are dyes which are preferably selected which otherwise are known to have good launderability from fabrics. When used in the composition of the invention, such dyes not only enhance washability from skin, but also enhance launderability from fabric as well. While certain coloring compositions containing polymeric dyes have been removed from skin and fabric with soap and a significant amount of rubbing, the erasable whiteboard compositions of the present invention can be rinsed off using water alone.

One suitable type of colorant for use in compositions of the present invention are acid dyes. By way of illustration, and not in limitation, acid dyes that have been found suitable for use in this invention are Acid Violet 12, Acid Green 3, Acid Blue 9, Acid Yellow 17, Acid Yellow 23, Acid Red 52 and Acid Red 388. Yellow F.D.& C. #6 may also be used.

15

20

25

30

10

15

20

25

30

35

Another category of suitable colorants for use in the present invention is polymeric dyes. Polymeric dyes are characterized as having polymeric chains covalently bonded to a chromophore molecule. By way of illustration, and not limitation, polymeric dyes suitable for use in compositions of the invention include Palmer Scarlet™, Palmer Blue™, Palmer Magenta™, and Experimental Palmer FL Red A 10TM. These polymeric dyes are commercially available from Milliken Chemical and may be covered by one or more of U.S. Patent Nos. 4,981,516, 5,043,013, and 5,059,244, the disclosures of which are incorporated herein by reference. Other polymeric dyes useful in the practice of the invention include polyalkyleneoxy-substituted chromophore compounds such as, for example, alkyleneoxy-substituted methine colorants. While certain coloring compositions containing polymeric dyes have been removed from skin by rubbing with soap and water, the coloring compositions of the present invention can be rinsed off using water alone. Also, the coloring compositions of the present invention can be easily washed off or more completely removed from many previously staining surfaces such as wallpaper, painted walls, wood, etc.

Another type of colorant suitable for use in the washable coloring compositions of the present invention is pigments. Examples of suitable pigments include inorganic pigments such as titanium dioxide or ferric oxide, or organic pigments such as carbon black, phthalocyanines (e.g., copper phthalocyanine blue), azo pigments, quinacridones, anthraquinones, dioxazines, indios, thioindios, perynones, perylenes, indolenones and azo-azomethines. Encapsulated pigments may also be utilized. To achieve good coloring and promote compatibility with the remaining ink components, the pigment may be utilized in the form of an aqueous dispersion, inasmuch as pigments are by definition insoluble materials. Pigment dispersions are commercially available which are combinations of a pigment, an aqueous based character, and a surfactant or dispersant system. A pigment dispersion may also be prepared specifically for use in the coloring compositions of the invention. From the standpoint of convenience, a commercial pigment dispersion is preferred for use in the present invention. Typical commercial dispersions contain 30 to 74% by weight active pigment ingredients. Examples of suitable pigment dispersions include Hostafine Rubine F6B (C.I. Pigment Red 184 dispersion), Blue B2G (Pigment Blue 15-3) and Black 7 (Pigment Black T), marketed by Hoechst Celanese Corporation under the tradename "Hostafines Dispersions."

The coloring compositions of the invention may contain polymeric dyes, acid dyes, pigments, or mixtures thereof. Additionally, the compositions may contain two or more polymeric dyes, two or more acid dyes, or two or more pigments to achieve the desired color. The colorant is preferably present in an amount of from about 2% to about 20% by weight of the total coloring composition of the invention. The minimum concentration of colorant which will produce a workable coloring composition is governed by the color intensity desired, though as little as 0.5% colorant may be sufficient for certain applications. The maximum workable concentration of colorant is determined largely by the ability to maintain a stable composition, and can vary widely depending upon the concentration of other components. The maximum amount of colorant is also a function of the characteristics of the desired end product, though a practical upper limit in the formulation of the composition of the invention as, for example, an erasable whiteboard marker ink, is about 30% by weight of the total coloring composition of the invention. Higher concentrations may cause board staining (i.e., ghosting), defeat washability and yield an undesirably high viscosity. For whiteboard applications, too much dye raises the viscosity and makes it difficult to add a sufficient amount of film forming resin and/or dyeblocker necessary to yield the desired washability. Preferably, the dry erase coloring composition should have a viscosity less than 6 cps when used as a marker ink.

When a commercial pigment dispersion is utilized, a practical limit is imposed on the concentration of pigment in the dispersion. The preferred concentration range for most applications is from about 1% to about 10% active pigment by weight of the coloring composition. A concentration of about 3% active pigment by weight is ordinarily required to ensure good coloration in a typical marker ink and most preferred is a concentration of active pigment in a range of about 1.5% to about 5% by weight of the coloring composition.

The coloring composition of the present invention also includes an amount of an aqueous or other dye vehicle effective to form a solution of the remaining components. The preferred dye vehicle is water. The maximum amount of dye vehicle is the amount which results in a stable composition and which is capable of forming a mark having the minimum acceptable visibility on a substrate. The minimum amount of water is that necessary to form a stable solution of the components of the coloring composition and provide a composition which can be freely dispensed from the selected dispensing element, where the composition is to

5

10

15

20

25

30

10

15

20

be used as a marker ink. Other suitable dye vehicles include alcohol or other water-miscible solvents, such as, for example, a 30% denatured alcohol solution. Compatible mixtures of water and alcohol or other water-miscible solvents may also be used as a dye vehicle. Suitable water/solvent dye vehicles may contain from 0% to 100% alcohol or other water-miscible solvents. Preferably, the dye vehicle may comprise from 0% to about 50% alcohol or other water-miscible solvents. The proportion of dye vehicle contemplated herein is from about 30% to about 90% by weight of the total coloring composition of the invention. Some or all of the water may be contributed by water found as a portion of one or more of the other components.

The coloring compositions of the invention may also contain a release agent. Where the coloring compositions of the invention are to be used to create marks on a whiteboard, the release agent itself forms a separating film between the surface of the whiteboard and the film forming resin. The film forming resin does not form on the surface of the board, but instead on top of the release agent. As a result, the film forming resin, containing the colorant, may be erased with a dry cloth or eraser. Typical release agents include, but are not limited to, siloxanes, such as polydimethylsiloxanes; polyethylene glycols; monobasic higher fatty carboxylic acid esters; mono- or diesters of dihydric alcohols, wherein the ester has a molecular weight of 100 or more; fatty acid triglycerides; higher hydrocarbons such as paraffin and squalene; polyesters and polyethers having molecular weights of 400 or more; and esters of a polycarboxylic acid with an alcohol.

The preferred release agents are polyalkylene oxide-modified

25 polydimethylsiloxanes sold under the trade name Silwet L-7230™ and Silwet L
7607™ by OSi Specialties, Inc. Other useful release agents include, but are not limited to, Silwet L-7608™ marketed by OSi Specialties, Inc., DCQ43667™ and FF400™ marketed by Dow Corning, Carbowax™ Polyethylene Glycol 1450 marketed by Union Carbide, and Lipopeg 4L™ marketed by Lipo Chemicals Inc.

30 Mixtures of these release agents may also be utilized in the dry erase coloring compositions of the present invention. The release agent contained in the erasable whiteboard marker ink composition is present in an amount of from about 1% to about 30% by weight of the total coloring composition and, preferably, in an amount of from about 5% to about 15% by weight of the total coloring compositions of composition. At a minimum, the release agent must be present in compositions of

WO 98/36031

5

10

15

20

25

30

35

the invention to be used on whiteboards in an adequate amount to produce compositions that can are easily erasable from the whiteboard. However, when excessive amounts of release agent are used, the composition has an excessively high viscosity, which may render the composition unsuitable for use in conventional markers.

The coloring compositions of the invention may optionally contain a resin which is water soluble and film forming at room temperature. When marks are formed using the composition of the invention including this film forming resin, and dried on an impervious writing surface, the marks have a continuous resin layer. The water soluble film forming resin also provides the coloring composition with a viscosity suitable for writing when the composition is used in the form of a whiteboard marker ink and helps to prevent staining of the whiteboard. It is also believed that the dyeblocker condensation product additives of the present invention may also serve as a film-former upon which the dye is deposited.

The preferred film forming resin for use in the present invention is polyvinylpyrrolidone sold under the trade name PVP K-15TM by GAF Chemicals Corporation. PVP K-15TM is typically supplied in 30% solution of polyvinylpyrrolidone (i.e., 70% water). Different molecular weight polyvinylpyrrolidone polymers, such as PVP K-30TM, and modified polyvinylpyrrolidone polymers, such as polyvinyl acetate-modified polyvinylpyrrolidone, may also be used. Additional useful film forming resins include, for example, but are not limited to, natural resins, such as gum arabic, rosin, or shellac; modified rosins such as rosin esters, hydrogenated rosins, rosin-modified maleic acid resins or rosin-modified phenol resins; various phenol-resins; cellulosic resins such as ethyl cellulose resins or acetyl cellulose resins; ketone resins, polyvinyl alcohol, polyvinyl acetate resins, petroleum resins, polyvinyl butyral resins, vinylpyrrolidone-vinyl acetate copolymer resins or polyacrylic acid ester resins. Mixtures of two or more of these film forming resins may also be employed in the present invention.

The film forming resin should be used in an effective amount. Preferably, the film forming resin is contained in the coloring composition suitable for use on whiteboards is present in an amount of from about 0% to about 10% by weight of the active film forming resin added of the total coloring composition and, preferably, in an amount of from about 1% to about 5% by weight of the active

10

15

20

25

30

film forming resin based on the total composition of the coloring composition of the invention. Where the film forming resin used is the polyvinylpyrrolidone supplied in solution as PVP K-15TM, from about 0% to about 30% by weight of the PVP K-15TM solution based on the total weight of the coloring composition may be used and, preferably, from about 5% to about 15% by weight of the PVP K-15TM solution is used based on the total weight of the coloring composition. The actual amount of film forming resin added to the coloring compositions of the invention depends upon the particular colorant used. When the amount of film forming resin is too large, the resultant dry erase coloring composition has an excessively high viscosity so that it writes poorly and, moreover, the writings formed therewith are not readily erased from a whiteboard.

Other film forming components may also be added to the dry erase coloring compositions of the present invention to provide enhanced washability. Suitable film forming components may include starches. A wide range of starches are suitable including, for example, warm water soluble starch and cold water soluble starch. Preferably, the starch may be added in an amount of from about 2% to about 30% by weight of the coloring composition to beneficially enhance washability. The combination of a dyeblocker and starch in the present invention enhances washability on skin, walls, wallpaper, wood and other surfaces.

One suitable starch for use in compositions of the present invention is Drisweet 42 manufactured by Hubinger Co. Dri-sweet 42 is a cold water soluble starch. Another suitable cold water soluble starch is ICB 3000 manufactured by Staley.

The dry erase coloring compositions of the invention are especially suitable for use as an erasable whiteboard marker ink in which the dye vehicle is water. The erasable whiteboard marker ink may be supplied in a delivery system, such as a marking instrument, to enable children to color or draw on impervious surfaces such as whiteboards. Suitable nibs for use in such a system are bonded fiber or sintered plastic nibs. A marking pen containing the dry erase coloring composition of the invention in the form of an ink may generally take the form of any conventional marker. Preferably, the marker uses a bonded fiber or sintered plastic nib. The marker reservoir containing the ink can be any standard marker delivery system including, but not limited to, acetate, polyester, or polypropylene fiber systems. In addition, a fiberless system may be used.

10

15

20

25

30

35

In a preferred embodiment of the invention, the coloring composition of the invention is in the form of an erasable whiteboard marker ink. The ink contains a colorant, water, a release agent, a film forming resin, and an anionic dyeblocker. Preferably, the dyeblocker additive is an aromatic organic sulfonate and, more preferably, it is selected from the group consisting of sulfonated naphthalene condensation products, a sulfonated phenol-formaldehyde condensation products, and mixtures thereof. This inventive whiteboard marker ink exhibits favorable dry erase characteristics from skin, fabric and other household surfaces.

Compositions of the present invention may, when in the form of an erasable marker ink, also advantageously include a humectant, a surfactant, a preservative, a defoamer, and/or a pH regulant. These materials and their functions are well known, and their mention here is by way of illustration only. Generally, any effective amount of the additive may be used so long as the stability of the coloring composition is not adversely affected and the composition is suitable for use in the desired end product.

For example, it may be possible to include a humectant in an erasable whiteboard marker ink to retard the evaporation of water from the ink solution. This avoids unduly rapid drying of the ink in the marker nib which can cause clogging of the nib and impair the function of the marker. Further, a humectant may improve freeze/thaw stability of the inventive ink compositions. Typical humectants include polyhydric alcohols such as glycerine, propylene glycol, ethylene glycol, and diethylene glycol, hydroxylated starches, low molecular weight (m.w. = 200-400) poly(ethylene glycols), and mixtures of these materials. Any effective amount of humectant may be used although a generally useful concentration range for these humectants is from about 5% up to about 30% by weight of the total coloring composition.

Surfactants in any effective amount (generally up to about 0.1% by weight) may also be included in the preferred erasable whiteboard marker ink compositions of the invention for the purpose of adjusting such properties as viscosity (for proper dispensing of ink through the nib), and surface tension (for good flow properties and nonporous surface wetting). Anionic surfactants, nonionic surfactants, such as poly (ethylene glycol) ether, alkylaryl polyether alcohol, fluorinated alkyl esters, and mixtures of such materials are preferred for use in the compositions of the invention when in the form of erasable whiteboard marker inks.

10

15

20

25

30

35

Preservatives of conventional types are also advantageously employed in the compositions of the invention to extend the shelf life of the composition. The preservative preferably serves as both a bactericide and a fungicide. Some typical preservatives useful in the present invention include methyl p-hydroxybenzoate, glutaraldehyde, hydroxybenzoic acid esters, 3-iodo-2-propynyl butyl carbamate, bicyclic oxazolidones, and a biocide comprising as the active ingredients 5-chloro-2-methyl-4-isothiazolin-3-one and, 2-methyl-4-isothiazolin-3-one.

Preservatives are usually effective when present in any effective amount but generally are present in amounts of from about 0.1% up to about 1% by weight. Preferred preservatives include Kathon PFMTM (isothiazolinones) manufactured by Rohm and Haas, and Nuosept 95TM (bicyclic oxazolidines solutions) manufactured by Huls America.

The pH of the coloring compositions of the present invention is preferably in the range of about 3.0 to about 10.0, more preferably about 4.0 to about 9.0. To maintain this pH, a pH regulant may be employed. Preferably, neutralized versene is used as a pH regulant. In addition to controlling pH, neutralized versene may also help ease the erasability of some dyes from whiteboards when compositions of the invention are used as whiteboard marker inks. The pH regulant may be added in an amount ranging from about 0% to about 20% by weight. In one preferred composition, the pH regulant, neutralized versene, is added in an amount of about 10% by weight of the total erasable whiteboard marker ink composition.

The coloring compositions of the present invention may also contain a defoamer to prevent foaming during mixture of the various components. Suitable defoamers include silicones and siloxanes. The preferred defoamer is Tego Foamax 800TM marketed by Goldschmidt Chemical Corp. Other suitable defoamers include Zerofome AF-200TM marketed by NuTech Corp., Surfynol DF58TM marketed by Air Products, and Foamaster HTM marketed by Henkel. The addition of defoamer to the coloring compositions of the present invention does not adversely affect either the removability from whiteboards or washability when the compositions are used as whiteboard marker inks. The amount of defoamer depends upon the amounts of other components present in the coloring composition, although typically about 0.1% to about 5% by weight of the total dry erase coloring composition is used.

The coloring compositions of the present invention can be prepared in any suitable manner. For example, polymeric dye, dye vehicle, release agent, film

forming resin, and anionic dyeblocker along with other optional components (e.g., preservatives and humectants) can be added to a suitable vessel and mixed until a suitable solution is obtained.

5 EXAMPLES

Examples of coloring compositions of the present invention are as follows. These examples further illustrate the present invention but, of course, should not be construed as in any way limiting its scope. Quantities are in percent by weight of the total composition. These example compositions are suitable for use in marking on whiteboards.

Different coloring compositions were prepared using acid and polymeric dyes and a dyeblocker condensation product additive. These compositions were formulated in the form of marker inks. These compositions containing a film forming resin, a release agent, and dyeblocker condensation product additive are set forth below in Examples 1-8. In examples 1-2 and 4-8, the dyeblocker additive is the sulfonated phenol-formaldehyde condensation product, Aerofix NTM. In example 3, the dyeblocker additive is the sulfonated naphthalene condensation product, Tamol SNTM.

20 Example 1 -- Red

10

15

	Component	<u>wt. %</u>
	Deionized water	52.54
25	(dye vehicle)	
	Palmer Scarlet	9.99
	(polymeric dye)	
	Palmer FL Red A10	2.00
	(polymeric dye)	
30	Aerofix N	19.97
	(phenol-formaldehyde condensat	
	PVP K-30 (30% solution)	5.14
	(film forming resin)	5.11
	Silwet L-7607	9.99
35	(release agent)	3.33
33	Nuosept 95	0.30
		0.30
	(preservative)	0.00
	Kathon PFM	0.08
	(preservative)	

BNSDOCID: <WO_____9836031A1_I_>

Example 2 -- Blue

	Component	<u>wt. %</u>
5	Deionized water (dye vehicle)	44.62
	Palmer Blue (polymeric dye)	5.00
	Aerofix N	20.00
10	(phenol-formaldehyde condensation	product)
	PVP K-15 (30% solution) (film forming resin)	10.00
	Silwet L-7607	10.00
15	(release agent) Neutralized versene	10.00
13	(pH regulant)	10.00
	Nuosept 95	0.30
	(preservative)	0.50
	Kathon PFM	0.08
20	(preservative)	, 0.00
	Example 3 Yellow	
25	Component	<u>wt. %</u>
	Deionized water	72.62
	(dye vehicle)	72.02
	Acid Yellow 23	2.00
30	(acid dye)	
	Tamol SN	5.00
	(naphthalene condensation product)	1000
	PVP K-15 (30% solution) (film forming resin)	10.00
35	Silwet L-7607	10.00
	(release agent)	10.00
	Nuosept 95	0.30
	(preservative)	. 0.50
	Kathon PFM	0.08
40	(preservative)	

Example 4 -- Green

•	Component	<u>wt. %</u>
5	Deionized water (dye vehicle)	55.62
	Palmer Blue (polymeric dye)	3.20
10	Acid Yellow 23 (acid dye)	0.80
10	Aerofix N	20.00
	(phenol-formaldehyde condensation p	
	PVP K-15 (30% solution) (film forming resin)	10.00
15	Silwet L-7607	10.00
	(release agent)	
	Nuosept 95	0.30
	(preservative) Kathon PFM	0.08
20	(preservative)	0.00
	Example 5 Black	
25	Component	<u>wt. %</u>
	Deionized water (dye vehicle)	39.82
	Palmer Blue	4.40
30	(polymeric dye) Palmer Magenta	4.40
	(polymeric dye) FD&C Yellow #6	1.00
0.5	(acid dye)	20.00
35	Aerofix N (phenol-formaldehyde condensation p	20.00
	PVP K-15 (30% solution)	10.00
	(film forming resin) Silwet L-7607	10.00
40	(release agent) Neutralized versene	10.00
	(pH regulant)	20.00
	Nuosept 95	0.30
45	(preservative) Kathon PFM	0.08
73	(preservative)	0.08
	<i>d</i>	

Example 6 -- Orange

	Component	<u>wt. %</u>
5	Deionized water (dye vehicle)	56.62
	FD&C Yellow #6 (acid dye)	3.00
10	Aerofix N	20.00
10	(phenol-formaldehyde condensation pro	duct)
	PVP K-15 (30% solution)	10.00
	(film forming resin)	
	Silwet L-7607	10.00
15	(release agent)	
13	Nuosept 95	0.30
	(preservative) Kathon PFM	
	(preservative)	0.08
	(preservative)	
20	Example 7 Violet	
	Component	<u>wt. %</u>
	Deionized water	46.42
25	(dye vehicle)	70.72
	Palmer Magenta	3.20
	(polymeric dye)	2.20
	Aerofix N	20.00
30	(phenol-formaldehyde condensation prod	luct)
30	PVP K-15 (30% solution)	10.00
	(film forming resin) Silwet L-7607	
	(release agent)	10.00
	Neutralized versene	10.00
35	(pH regulant)	10.00
-	Nuosept 95	0.30
	(preservative)	0.50
	Kathon PFM	0.08
	(preservative)	0.00
40	-	

PCT/US98/02682

Example 8 -- Brown

	Component	<u>wt. %</u>
5	Deionized water	42.06
	(dye vehicle) Palmer Blue	0.88
	(polymeric dye)	0.00
	FD&C Yellow #6	1.00
10	(acid dye)	
	Palmer Scarlet	5.68
	(polymeric dye)	
	Aerofix N	20.00
	(phenol-formaldehyde condensati	ion product)
15	PVP K-15 (30% solution)	10.00
	(film forming resin)	
	Silwet L-7607	10.00
	(release agent)	
	Neutralized versene	10.00
20	(pH regulant)	
	Nuosept 95	0.30
	(preservative)	
	Kathon PFM	0.08
	(preservative)	

25

TEST PROCEDURES

19

A. <u>Skin Fugitivity</u>

The fugitivity from skin of the compositions of the invention cited in the above examples was measured by the following test:

1. Wash hands with soap and warm water. The pre-stain cleansing removes excess oil and dirt from the skin and provides a more consistent skin surface for testing. Allow the skin to dry for 30 seconds.

35

- 2. With the compositions of the invention used in a marker having a sintered plastic nib, draw a stripe on the palm of the hand with the flat side of the nib. In the usual case, a 1/4 inch wide by 1 inch long stripe works well. Apply enough pressure and/or multiple passes to develop a stripe with good color intensity. If it is desired to make a comparison among two or more compositions, more than one stripe may be drawn. Let stripes dry for fifteen minutes.
- 3. In the case of a marker, place hand under tap and briefly rinse off excess ink with warm water.

4. Wash hands with Ivory brand bar soap in the following manner: lather using a minimum amount of soap; replace soap in soap dish; rub hands together briskly with modest pressure for 30 seconds; rinse away soap.

5

5. Wipe hands dry with paper towels, and complete the drying with a relatively dry towel. A dry towel will help to rub off residual traces of ink.

B. Fabric Fugitivity

The fugitivity from fabric of the compositions of the invention was measured by the following test.

- Pre-wash test fabrics with bleach, non-staining water softener and ordinary household phosphate detergent powder using 120°F hot water as directed in ASTM D4265-83, and dry.
 - 2. Cut test swatches of pre-washed fabrics to be tested.
- 3. Deposit marker inks onto fabric swatches and allow to dry for 4 20 hours.
 - 4. Staple a group of stained swatches to the edges of a bath towel.
- 5. Add a dummy load of unstained fabrics to provide a four pound wash load. Wash the load in a washing machine for 12 minutes with a warm (about 80°F to about 90°F)/cold cycle or a cold (about 35°F to about 55°F)/cold cycle.
 - 6. Dry the load in a dryer.

30

7. Detach the test swatches from the carrier towel, iron, and observe degree of staining.

15

EVALUATION OF TEST DATA

Skin and fabric fugitivity data are based on a visual rating system as follows:

0 = no stain
0.5 = very light stain
1 = light stain
2 = light to moderate

2 = light to moderate stain

3 = moderate to heavy stain

4 = heavy stain

An asterisk (*) following the numerical rating denotes that particular degree of staining after only a water rinse instead of after rubbing with soap and water.

The viscosity, pH and skin fugitivity of the coloring compositions in Examples 1-8 is set forth in Table I. Skin fugitivity was measured on 14 individuals. As washability results will vary by individual, the range of observed skin fugitivity for each of the coloring compositions examples is provided.

TABLE I -- Skin Fugitivity

20	Example Number	viscosity (cps)	pН	Skin Fugitivity
	1	5.33	8.20	0, 0*, 0.5* 0, 0*, 0.5, 0.5*, 1 0, 0.5, 0.5*
	2	4.17	7.95	0, 0, 0, 0.5, 0.5, 1
•	3	3.17	7.50	0, 0.5, 0.5*
25	4	3.76	8.05	0, 0*
	5	5.56	8.00	0, 0*
	6	4.05	8.40	0, 0*, 0.5, 0.5* 0, 0*, 0.5*
	7	4.57	8.19	0, 0*, 0.5*
	8	5.25	8.15	0, 0

30

35

The fabric fugitivity data of the coloring compositions in Examples 1-8 is set forth in Table II. The washability of these inks was tested on 50% cotton/50% polyester blends and 100% cotton. Additionally, washability was examined using a washing machine with both a cold/cold cycle and a warm/cold cycle. The cold/cold cycle was repeated on the fabric samples. As demonstrated, no stains were observed on either the 50% cotton/50% polyester blend or the 100% cotton samples after a second cold wash. For comparison, the fugitivity from fabric of a control coloring composition was analyzed. The control is a typical alcohol-based whiteboard ink composition.

TABLE II -- Fabric Fugitivity

						_				
		<u>Ex 1</u>	<u>Ex 2</u>	<u>Ex 3</u>	<u>Ex 4</u>	<u>Ex 5</u>	<u>Ex 6</u>	<u>Ex 7</u>	<u>Ex 8</u>	<u>Cntrl</u>
5	50%/50% Blend (1st cold cycle)	1.5	0	1	1	1	0.5	0.5	0.5	4
	50%/50% Blend (2nd cold cycle)	0	0	0	0	0	0	0	0	3.5
10	100% Cotton (1st cold cycle)	2	0	1	1	1.5	0.5	1.5	1	4
15	100% Cotton (2nd cold cycle)	0.5	0	0	0	0	0	0	0	3.5
	50%/50% Blend (warm cycle)	0	0	0	0	0	0	0.	0	4
20,	100% Cotton (warm cycle)	0	0	0	0	0	0	0	0	4

From the foregoing Examples 1-8, it can be seen that the dry erase coloring compositions of the present invention containing a dyeblocker exhibit enhanced fugitivity from skin and fabric.

Coloring compositions of the invention containing a dyeblocker condensation product additive other than Aerofix N are set forth below in Examples 9-12. Examples 13-16 and 18 below illustrate coloring compositions of the invention that do not contain a film forming resin. Each of these examples is in the form of a marker ink. Example 17 is illustrative of a dry erase coloring composition using a dye vehicle comprising a mixture of water and alcohol. Example 18 is illustrative of a marker ink containing a starch.

BNSDOCID: <WO_____9836031A1_I_>

	Component	<u>wt. %</u>
5	Deionized water (dye vehicle)	64.62
	Palmer Blue (polymeric dye)	5.00
10	Intratex N	5.00
10	(phenol-formaldehyde condensation pro- PVP K-15 (30% solution)	15.00
	(film forming resin)	15.00
	Silwet L-7607	10.00
15	(release agent) Nuosept 95	0.30
13	(preservative)	0.50
	Kathon PFM	0.08
	(preservative)	
20		
	Example 10	
	Component	<u>wt. %</u>
25	Deionized water	68.87
	(dye vehicle) Acid Blue 9	1.25
	(acid dye)	1.23
	Gascofix NY	12.00
30	(phenol-formaldehyde condensation prod	duct) 10.00
	PVP K-15 (30% solution) (film forming resin)	10.00
	Silwet L-7608	7.50
35	(release agent)	0.30
JJ	Nuosept 95 (preservative)	0.30
	Kathon PFM	0.08
	(preservative)	•

	Component	wt. %
5	Deionized water (dye vehicle)	81.37
	Acid Yellow 23	2.00
10	(acid dye) Tamol SN	5.00
10	(naphthalene condensation product) PVP-VA	3.00
	(film forming resin) Silwet L-7607	8.00
15	(release agent) Dow Corning FC 120	0.25
	(surfactant) Nuosept 95	0.30
20	(preservative) Kathon PFM	0.08
20	(preservative)	
	Example 12	
25	Component	<u>wt. %</u>
	Deionized water	63.82
20	(dye vehicle) Palmer Blue	4.40
30	(polymeric dye) Palmer Magenta	4.40
	(polymeric dye) FD&C Yellow #6	1.00
35	(acid dye) Tamol SN	5.00
	(naphthalene condensation product) PVP K-30 (30% solution)	4.00
	(film forming resin) Neutralized versene	5.00
40	(pH regulant) Lipopeg 4L	12.00
	(release agent) Nuosept 95	0.30
45	(preservative) Kathon PFM	0.08
	(preservative)	0.00

	Component	<u>wt. %</u>
5	Deionized water (dye vehicle)	38.72
	Palmer Blue (polymeric dye)	0.90
10	Palmer Scarlet	5.70
10	(polymeric dye) FD&C Yellow #6	1.00
	(acid dye) Aerofix N	25.00
15	(phenol-formaldehyde condensation prod Dow Corning FF400	8.00
	(release agent) Neutralized versene (pH regulant)	10.00
20	Glycerine	10.00
20	(humectant) Nuosept 95	0.30
	(preservative) Kathon PFM	0.08
25	(preservative) Tego Foamex 800 (defoamer)	0.30
	Example 14	
30	Component	<u>wt. %</u>
	Deionized water	54.82
2.5	(dye vehicle) Palmer Blue	4.40
35	(polymeric dye) FD&C Yellow #6	1.00
	(acid dye)	
	Palmer Magenta	4.40
40	(polymeric dye)	
40	(polymeric dye) Aerofix N (phenol-formaldehyde condensation prod Dow Corning Q43667	20.00
	(polymeric dye) Aerofix N (phenol-formaldehyde condensation prod Dow Corning Q43667 (release agent) Neutralized versene	20.00 uct)
40 45	(polymeric dye) Aerofix N (phenol-formaldehyde condensation prod Dow Corning Q43667 (release agent) Neutralized versene (pH regulant) Nuosept 95	20.00 uct) 5.00
	(polymeric dye) Aerofix N (phenol-formaldehyde condensation prod Dow Corning Q43667 (release agent) Neutralized versene (pH regulant)	20.00 uct) 5.00

	Component	<u>wt. %</u>
5	Deionized water (dye vehicle)	64.62
	Palmer Blue (polymeric dye)	5.00
10	Aerofix N (phenol-formaldehyde condensation pro- Silwet L-7607	
	(release agent)	4.00
	Silwet L-7608 (release agent)	6.00
15	Neutralized versene (pH regulant)	10.00
	Nuosept 95 (preservative)	0.30
20	Kathon PFM (preservative)	80.0
	Example 16	
25	Component	wt. %
	Deionized water (dye vehicle)	69.62
30	FD&C Yellow #6 (acid dye)	3.00
	Aerofix N (phenol-formaldehyde condensation prod	20.00 luct)
	Silwet L-7230 (release agent)	5.00
35	PÈG 400 (humectant)	2.00
	Nuosept 95 (preservative)	0.30
40	Kathon PFM (preservative)	0.08

T	. 1 _	17
Exam	nie	1/
~//*****	~~~	

	Component	<u>wt. %</u>
5	Deionized water (dye vehicle)	35.62
	Denatured ethanol	30.00
10	(dye vehicle) Palmer Blue	5.00
10	(polymeric dye) Aerofix N	16.00
	(phenol-formaldehyde conden	
	PVP K-15 (30% solution)	8.00
	(film forming resin)	
15	Silwet L-7607	5.00
	(release agent)	10.00
	Neutralized versene (pH regulant)	10.00
	Nuosept 95	0.30
20	(preservative)	
	Kathon PFM	0.08
	(preservative)	
	Example 18	
25	Component	<u>wt. %</u>
	Deionized water	61.62
	(dye vehicle) Palmer Blue	5.00
30	(polymeric dye)	5.00
	Dowfax 8390	3.00
	(dyeblocker additive)	15.00
	Dri-sweet 42	15.00
35	(starch) Silwet L-7607	15.00
	(release agent)	
	Nuosept 95	0.30
	(preservative)	Λ Λο
40	Kathon PFM (preservative)	0.08
TU	(preservative)	

In another aspect of the present invention, the image produced on a whiteboard or other non-porous surface such as plastic laminate using the inventive coloring compositions can be transferred to paper. Surprisingly, it has been found that images formed using the inventive compositions can be easily transferred to paper to produce beautiful color prints. In general, the inventive printing process involves the following steps: (a) drawing on a whiteboard or other non-porous surface to generate an image; (b) applying a moistened paper to the

10

15

20

25

.30

35

image; (c) rubbing the moistened paper to transfer the image from the whiteboard or other non-porous surface to the paper; and (d) removing the paper from the whiteboard or other non-porous surface. In this manner, a color print on paper is produced from the original drawing.

The drawing on the whiteboard or other non-porous surface may be created with the washable coloring compositions of the present invention described above. Following the drawing of an image on a whiteboard or other non-porous surface, a piece of paper is prepared to which the image will be transferred. The paper is moistened with water or other water-based emulsion or gel such as a lotion such as that marketed under the name LUBRIDERM. The paper can be moistened in any manner including, but not limited to, using a spray bottle, a damp sponge, a paint roller or flat spreading blade. Moreover, the amount of water or water based emulsion or gel added to the paper may be varied to produce different effects on the color print. Thus, the paper can be slightly moistened or fully moistened depending on the desired effect. Various paper stocks can be used in the inventive printing process. Paper stocks sold under the name Cascade-9000 (manufactured by Boise Cascade) produce excellent results in forming a color print from the whiteboard image.

Optionally, in the event that excessive moisture is added to the paper, the excess water may be removed. Removal may be accomplished, for example, by using an flat spreading blade such as an automotive putty spreader or a paper towel to blot dry the paper. Generally, moisture should be removed from the moistened paper such that there are no "shiny" spots left.

The moistened piece of paper is then placed over the image on the whiteboard or other non-porous surface. The transfer of the image to the paper is completed by rubbing over the surface of the paper. The rubbing step may be accomplished using, for example, the user's hands, a roller or flat spreader blade such as an automotive putty blade. Preferably, to ensure proper transfer of the image, the moistened paper is left on the surface of the whiteboard or other non-porous surface for at least about 30 seconds after being applied. Finally, the paper is removed from the surface to produce a color print of the original image which has been transferred to paper.

The quality of the color print produced by the inventive process is affected by several factors during the transfer process including the level of moisture present in the paper, removal of any excess water from the paper, and the pressure applied to the paper during the rubbing step. To produce a clear color print without smearing the image, one or more of the following adjustments may be made: (1) use less water to moisten the paper; (2) remove any excess water present on the paper; or (3) apply less pressure during the rubbing phase.

In the event that the inventive process does not produce a complete color print, the transfer process may be repeated one or more times. For example, if there are light spots on the paper where the original image has not completely been transferred, then the following steps may be followed: (a) reapply the paper to the whiteboard or other non-porous surface bearing the original drawing ensuring registration of the print with the original drawing; (b) rub the paper surface to transfer the remainder of the original image; and (c) remove the paper from the whiteboard or other non-porous surface.

The inventive process may be used to transfer an image from any whiteboard or other non-porous surface to which the coloring compositions of the present invention are applied. Optionally, a special whiteboard with dowel pins along one edge of the whiteboard may be used on which common three-hole punched paper may be mounted. This special whiteboard permits registration of three-hole punched paper over the image in the same position each time and, therefore, is especially useful if the image is not completely transferred to the paper on the first attempt. Following the first transfer attempt, the three-hole punched paper with a partial image can be remounted on the dowel pins in registration with the image such that the portions of the image remaining on the whiteboard may be transferred to the paper to form the complete original drawing.

In another embodiment of the invention, a white board or other sturdy base is constructed with an engaging device such as pegs or other suitable devices such as engaging slots for engaging and positioning the moistened paper such that the paper is maintained in a stable position. The engaging device may be in the form of one or more pegs extending from a flat surface of the base such that the pegs correspond to hole positions commonly found in paper or to hole positions which may be punched in the paper using a common hole punch. Common peg positions would match the typical two or three-hole punch devices typically commercially available.

In this embodiment, a piece of paper would be attached to the sturdy base by, for instance, hanging three-hole punched paper on three spaced pegs. A drawing could then be made using the inventive coloring compositions of the

5

10

15

20

25

30

10

15

20

present invention on a non-porous surface of a sheet of material such as paper covered with plastic laminate. The paper hanging on the sturdy base would then be moistened as described above. The original image on the non-porous surface would then be applied to the moistened paper by trapping the paper between the sturdy base and the non-porous surface. The reverse side of the non-porous surface is robbed to transfer the image to the paper. Then, the sheet of material having the non-porous surface is removed leaving the image on the paper. In this case, the sheet of material having the non-porous surface could also have three corresponding holes matching the pegs on the sturdy base to provide repeated registration between the original image on the second non-porous surface and the transferred image on the moistened paper.

All of the references cited herein, including patents, patent applications, and publications, are hereby incorporated in their entireties by reference.

While this invention has been described with an emphasis upon preferred embodiments, it will be obvious to those of ordinary skill in the art that variations of the preferred embodiments may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications encompassed within the spirit and scope of the invention as defined by the following claims.

WHAT IS CLAIMED IS:

- 1. A washable coloring composition comprising:
 - (a) one or more colorants selected from the group consisting of an acid dye, a polymeric dye, a pigment, and mixtures thereof;
 - (b) a dye vehicle;
 - (c) a release agent; and
 - (d) an anionic dyeblocker in an amount sufficient to enhance the fugitivity of said composition from skin and fabric.

10

- 2. The washable coloring composition according to claim 2, wherein said anionic dyeblocker is an aromatic organic sulfonate.
- 3. The washable coloring composition according to claim 1, wherein said aromatic organic sulfonate is selected from the group consisting of a sulfonated naphthalene condensation product, a sulfonated phenol-formaldehyde condensation product, and mixtures thereof.
- 4. The washable coloring composition according to claim 1, further comprising a film forming resin.
 - 5. The washable coloring composition according to claim 1, wherein said coloring composition is suitable for use on whiteboards.
- 25 6. The washable coloring composition according to claim 1, wherein said dye vehicle is selected from the group consisting of water, alcohol, and mixtures thereof.
- 7. The washable coloring composition according to claim 6, wherein said dye vehicle comprises from 0% to about 50% alcohol.
 - 8. An erasable whiteboard marker ink comprising:

- (a) a colorant selected from the group consisting of an acid dye, a polymeric dye, a pigment, and mixtures thereof;
- (b) water;
- (c) a release agent; and
- 5 (d) an anionic dyeblocker in an amount sufficient to enhance the fugitivity of said composition from skin and fabric.
 - 9. The erasable whiteboard marker ink according to claim 8, wherein said anionic dyeblocker is an aromatic organic sulfonate.
- 10
- 10. The erasable whiteboard marker ink according to claim 8, wherein said aromatic organic sulfonate is selected from the group consisting of a sulfonated naphthalene condensation product, a sulfonated phenol-formaldehyde condensation product, and mixtures thereof.
- 15
- 11. The erasable whiteboard marker ink according to claim 8, further comprising a film forming resin.
- 12. The erasable whiteboard marker ink according to claim 11, wherein said film forming resin is present in an amount of from about 1% to about 10% by weight of active film forming resin in said composition, said release agent is present in an amount of from about 2% to about 30% by weight of said composition, and said anionic dyeblocker is a sulfonated phenol-formaldehyde condensation product present in an amount of from about 2% to about 15% by weight of said composition.
 - 13. A washable dry erase coloring composition comprising:
 - (a) one or more colorants selected from the group consisting of a pigment, an acid dye, a polymeric dye, and mixtures thereof;
- 30 (b) a dye vehicle;
 - (c) a release agent; and
 - (d) an anionic dyeblocker in an amount sufficient to enhance the fugitivity of said composition from skin and fabric.
- 35 14. The washable dry erase coloring composition according to claim 13,

wherein said anionic dyeblocker is an aromatic organic sulfonate.

- 15. The washable dry erase coloring composition according to claim 14, wherein said aromatic organic sulfonate is selected from the group consisting of a sulfonated naphthalene condensation product, a sulfonated phenol-formaldehyde condensation product, and mixtures thereof.
- 16. The washable dry erase coloring composition according to claim 13, further comprising a film forming resin.

17. The washable dry erase coloring composition according to claim 13, wherein said dye vehicle is selected from the group consisting of water, alcohol,

- 15 18. The washable dry erase coloring composition according to claim 17, wherein said dye vehicle comprises from 0% to about 50% alcohol.
 - 19. An erasable whiteboard marker comprising a marker barrel, an ink and a nib, said ink comprising:
- 20 (a) one or more colorants selected from the group consisting of an acid dye, a polymeric dye, a pigment, and mixtures thereof;
 - (b) water;

and mixtures thereof.

- (c) a film forming resin;
- (d) a release agent; and
- 25 (e) an anionic dyeblocker in an amount sufficient to enhance the fugitivity of said composition from skin and fabric.
 - 20. The erasable whiteboard marker according to claim 19, wherein said anionic dyeblocker is an aromatic organic sulfonate.
 - 21. The erasable whiteboard marker according to claim 20, wherein said aromatic organic sulfonate is selected from the group consisting of a sulfonated naphthalene condensation product, a sulfonated phenol-formaldehyde condensation product, and mixtures thereof

35

10

15

20

25

- 22. An erasable whiteboard marker according to claim 19, wherein said nib is selected from the group consisting of bonded fiber nibs and sintered plastic nibs.
- 23. An aqueous erasable whiteboard ink composition suitable for use in a marking instrument, said composition comprising:
 - (a) one or more colorants selected from the group consisting of an acid dye, a polymeric dye, a pigment, and mixtures thereof:
 - (b) a film forming resin in an amount of from about 1% to about 10% by weight of active film forming resin of the total composition;
 - (c) a release agent in an amount of from about 2% to about 30% by weight of the total composition;
 - (d) a preservative in an amount of from about 0.1% to about 1% by weight of the total composition;
 - (e) an aromatic organic sulfonate in an amount of from about 2% to about 15% by weight of total composition.
- 24. A method of imparting skin and fabric fugitivity to a dry erase coloring composition containing an acid dye, polymeric dye or pigment, comprising adding to said composition an aromatic organic sulfonate dyeblocker selected from the group consisting of a sulfonated naphthalene condensation product, a sulfonated phenol-formaldehyde condensation product, and mixtures thereof in an amount sufficient to enhance the fugitivity of said composition from skin and fabric.
- 25. A method of transferring an image from a whiteboard or non-porous surface to paper, which method comprises:
 - (a) drawing on said whiteboard or non-porous surface to create said image with a washable coloring composition comprising:
 - (i) one or more colorants selected from the group consisting of an acid dye, a polymeric dye, and mixtures thereof:
 - (ii) a dye vehicle;
 - (iii) a release agent; and
 - (iv) an anionic dyeblocker in an amount sufficient to enhance the fugitivity of said composition from skin and fabric;
- (b) applying a moistened paper to said image on said whiteboard or
 35 non-porous surface;

15

- (c) rubbing said paper to transfer said image from said whiteboard or non-porous surface to said paper; and
 - (d) removing said paper from said whiteboard or non-porous surface.
- 5 26. The method of claim 25, wherein said anionic dyeblocker is an aromatic organic sulfonate.
 - 27. The method of claim 25, wherein said aromatic organic sulfonate is selected from the group consisting of a sulfonated naphthalene condensation product, a sulfonated phenol-formaldehyde condensation product, and mixtures thereof.
 - 28. The method of claim 25, wherein said washable coloring composition further comprises a film forming resin.

29. The method of claim 25, wherein said paper is slightly moistened.

- 30. The method of claim 25, wherein said paper is fully moistened.
- 20 31. The method of claim 25, which further comprises removing excess water from said paper prior to the application of said paper to said whiteboard or non-porous surface.
- 32. The method of claim 25, wherein said paper is left on said whiteboard or non-porous surface for at least 30 seconds.
 - 33. The method of claim 25, wherein said whiteboard or non-porous surface includes means for maintaining said paper in a stationary position.
- 30 34. A method of transferring an image from a non-porous surface to paper, which method comprises:
 - (a) drawing on said surface to create said image with a washable coloring composition comprising:
- (i) one or more colorants selected from the group consisting of an acid dye, a polymeric dye, and mixtures thereof;

- (ii) a dye vehicle;
- (iii) a release agent; and
- (iv) an anionic dyeblocker in an amount sufficient to enhance the fugitivity of said composition from skin and fabric;
- 5 (b) applying said image on said surface to a moistened paper positioned on a sturdy base;
 - (c) rubbing the side of said non-porous surface opposite the side carrying said image to transfer said image from said non-porous surface to said paper; and
- 10 (d) removing said non-porous surface from said paper.
 - 35. The method of claim 34, wherein said anionic dyeblocker is an aromatic organic sulfonate.
- 15 36. The method of claim 34, wherein said aromatic organic sulfonate is selected from the group consisting of a sulfonated naphthalene condensation product, a sulfonated phenol-formaldehyde condensation product, and mixtures thereof.
- 20 37. The method of claim 34, wherein said washable coloring composition further comprises a film forming resin.
 - 38. The method of claim 34, wherein said sturdy base includes means for engaging said paper to maintain said paper in a stationary position.

INTERNATIONAL SEARCH REPORT

In. ational Application No PCT/US 98/02682

A. CLASSI IPC 6	FICATION OF SUBJECT MATTER C09D11/16 B44C1/175	•	
According to	o International Patent Classification(IPC) or to both national classifica	tion and IPC	
	SEARCHED		
Minimum de IPC 6	ocumentation searched (classification system followed by classification CO9D B44C	n symbols)	
Documenta	tion searched other than minimumdocumentation to the extent that su	uch documents are included in the fields sea	arched
Electronic	data base consulted during the international search (name of data bas	se and, where practical, search terms used)	·
C. DOCUM	ENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the rele	vant passages	Relevant to claim No.
Υ	WO 90 12067 A (BINNEY & SMITH INC October 1990	.) 18	1-23
X	see claims 1-18,21,22,25		24
Y	EP 0 557 115 A (BINNEY & SMITH IN August 1993	IC.) 25	1–23
X	see claims 1-15,17,19		24
Y	EP 0 584 735 A (SAKURA COLOR PROD March 1994 see abstract & US 5 412 021 A cited in the application	OUCTS) 2	1–23
Y	EP 0 322 805 A (SAKURA COLOR PRODUCTS) 5 July 1989 see abstract		1–23
X Furt	ther documents are listed in the continuation of box C.	X Patent family members are listed l	n annex.
	atenories of cited documents :	"T" later document published after the inte	mational filing date
"A" document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention			
filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) cannot be considered novel or cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the			
"O" document referring to an oral disclosure, use, exhibition or other means document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family			us to a person skilled
	actual completion of theinternational search	Date of mailing of the international sea	urch report
2	88 May 1998	05/06/1998	
Name and	mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswlik	Authorized officer	
	Tel. (+31-70) 340-2040, Tx. 31 651 epo ni, Ear: (+31-70) 340-3016	Girard, Y	,

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Int. ational Application No PCT/US 98/02682

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT						
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.				
Α	GB 2 040 808 A (TRANSPARENT PAPER) 3 September 1980 see abstract	25				
		-				
·						
·						

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. (Ional Application No PCT/US 98/02682

Patent document cited in search repo		Publication date		ent family ember(s)	Publication date
WO 9012067	Α	18-10-1990	AU US	5437890 A 5116410 A	05-11-1990 26-05-1992
EP 557115	Α	25-08-1993	AU CA	3318293 A 2090057 A	26-08-1993 21-08-1993
EP 584735	A	02-03-1994		6122849 A 7053906 A 69300951 D 69300951 T 5412021 A	06-05-1994 28-02-1995 18-01-1996 08-08-1996 02-05-1995
EP 322805	A	05-07-1989	JP JP JP JP DE US US	2133477 A 2706959 B 1252681 A 2097986 C 7119383 B 3871512 A 5561175 A 5677363 A 5004763 A	22-05-1990 28-01-1998 09-10-1989 02-10-1996 20-12-1995 02-07-1992 01-10-1996 14-10-1997 02-04-1991
GB 2040808	Α	03-09-1980	NONE		

Form PCT/ISA/210 (patent family annex) (July 1892)

THIS PAGE BLANK (USPTO)